

# Fragility in soft colloidal IPN microgels

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Microgel particles of Interpenetrated Polymer Network (IPN) of PNIPAM and PAAc in D<sub>2</sub>O, have been investigated through dynamic light scattering (DLS) as a function of temperature, pH and concentration. The dynamics of the system is slowed down under H/D isotopic substitution due to the different balance between polymer/polymer and polymer/solvent interactions for the two solvents suggesting the crucial role played by H-bondings. A reduced swelling capability with respect to PNIPAM and water is found depending on pH. An Arrhenius and super-Arrhenius behavior of the structural relaxation time versus concentration has been found, respectively below and above the Volume Phase Transition and a fragility plot has been derived. Fragility can be tuned by temperature: particles undergo a transition from soft to stiff across the VPT, associated to increasing values of fragility. Soft particles have strong behavior, while stiff particles are fragile, with values dependent on the solvent above the VPT.

## 1 introduction

Research on colloidal systems has attracted great interest in the last years, due to the variety of their technological applications and to the richness of their phase behavior, which has provided new insights into glass transition. Indeed they are very good model systems for understanding the general problem of dynamic arrest, due to their larger tunability with respect to atomic and molecular glasses<sup>1–4</sup>. The typical size of the constituent particles makes colloids experimentally more accessible, since they can be easily investigated through conventional techniques, such as dynamic light scattering (DLS) and optical microscopy. Moreover their interparticle potential can be controlled by tuning external parameters such as packing fraction, waiting time and ionic strength, thus leading to complex phase diagrams with different arrested states (such as gels<sup>5–7</sup> and glasses<sup>8,9</sup>) and unusual glass-glass transitions<sup>10–12</sup>.

In particular among colloidal systems, soft colloids represent an interesting class of glass-formers, since, at variance with hard-sphere-like colloids, they are characterized by an interparticle potential with a finite repulsion at or beyond contact. As a result of the particle softness, a complex phase behavior has been pre-

dicted<sup>13–15</sup> and not yet experimentally reproduced. Moreover, it has been recently shown<sup>16</sup> that soft colloids exhibit the same wide variation of the structural relaxation time observed for supercooled molecular liquids approaching to the glassy state. This variation is characterized by the unifying concept of fragility, which gives a "universal" description of dynamic arrest in glass-forming liquids<sup>17–19</sup>. For "fragile" liquids, relaxation time is highly sensitive to changes in temperature, while "strong" liquids show a much lower sensitivity. For colloidal suspensions fragility must be defined replacing the inverse of temperature with concentration<sup>16,19,20</sup>. Hard-sphere colloidal suspensions are fragile and the absence of a wider range of fragility limits their versatility as a model system of the glass transition. Interestingly, for deformable soft colloidal particles, fragility is affected by their elastic properties, giving rise to strong behavior<sup>17,21</sup> and allowing to obtain the equivalent effect of molecular systems<sup>18</sup>. Nevertheless, many efforts have been for understanding the influence of the softness of the interparticle potential on the fragility of glass formers<sup>19,22–24</sup>, with controversial results between computer simulations<sup>23,24</sup> and experimental observations<sup>16</sup>.

In this framework microgels (aqueous dispersions of nanometre- or micrometre-sized hydrogel particles), repulsive-soft colloids<sup>25–27</sup>, allow to change their effective volume fraction and their elastic properties by tuning their response to an external stimulus. In particular they may exhibit high sensitivity to changes of pH, temperature, electric field, ionic strength, solvent or to external stresses or light pulses. These easily accessible external parameters allow to modulate the interparticle potential and their reversible Volume-Phase Transition (VPT) (swelling/shrinking be-

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havior), giving rise to novel phase-behaviors, drastically different from those of conventional hard-spheres-like colloidal systems<sup>26–30</sup>. Moreover these attractive smart materials<sup>31–34</sup> can be very useful for many applications in several fields, as agriculture, construction, cosmetics and pharmaceuticals, artificial organs and tissue engineering<sup>35–38</sup>.

One of the most studied responsive microgel is based on poly(N-isopropylacrylamide) also known as PNIPAM, a thermo-sensitive polymer. PNIPAM microgels were investigated for the first time in 1986 by Robert Pelton and Philip Chibante<sup>39</sup>, since then they have been widely studied both experimentally and theoretically and a clear picture of preparation, characterization and applications has been provided<sup>31,32,34,40,41</sup>.

PNIPAM microgels responsiveness is strongly dependent on the thermo-sensitivity of NIPAM polymer that presents a Lower Critical Solution Temperature in water at about 305 K. At room temperature indeed, the polymer is hydrophilic and strongly hydrated in solution, while it becomes hydrophobic above 305 K, where a coil-to-globule transition takes place. This gives rise to a Volume-Phase Transition from a swollen to a shrunken state of any microgel based on NIPAM polymer<sup>42</sup>. Moreover it has been shown that this typical swelling/shrinking transition is the driving mechanism of the phase behavior of aqueous suspensions of PNIPAM microgels, since it affects the interactions between particles, thus providing a good tunability of both softness and volume as a function of temperature<sup>16,25–27</sup>. Although a preliminary phase diagram<sup>26,28,30</sup> and important details on the gel structure of PNIPAM microgels near the volume phase transition have been obtained<sup>43,44</sup>, nevertheless the PNIPAM microgel behavior is far from being completely clear. In particular the understanding of its phase behavior at high temperatures and concentrations, where the formation of an attractive glass has been reported<sup>28</sup>, is still lacking. Furthermore it has been recently shown that the microgel swelling/shrinking behavior can be strongly affected by concentration<sup>28,45</sup>, solvents<sup>46</sup> and synthesis procedure (such as growing number of cross-linking points<sup>47,48</sup>, different reaction pH conditions<sup>49</sup> or by introducing additives into the PNIPAM network<sup>50</sup>).

In this context PNIPAM microgels containing another specie as co-monomer or interpenetrated polymer are even more interesting, as a more complex scenario can show up. In particular, addition of poly-acrylic acid (PAAc) to PNIPAM microgel provides pH-sensitivity to the thermo-responsive microgel. Also these systems undergo a volume phase transition with temperature, although with a remarkable reduction of their swelling capability with increasing AAc concentration<sup>51,52</sup>. Indeed the VPT of these microgels strongly depends on the effective charge density, controlled by the content of AAc monomer<sup>51,52</sup>, on the pH of the suspension<sup>53–58</sup> and on salt concentration<sup>53,59</sup>.

In this framework the synthesis procedure plays a crucial role, being the response of PNIPAM/PAAc microgels strictly related to the mutual interference between the two monomers. Indeed for randomly copolymerized PNIPAM/PAAc microgels (PNIPAM-co-AAc)<sup>53,54,56,59–63</sup>, the volume phase transition temperature (VPTT) increases with PAAc concentration. On the contrary, interpenetration of hydrophilic PAAc into the PNIPAM microgels network (IPN PNIPAM-PAAc)<sup>51,55,64–67</sup>, hereafter labelled as IPN mi-

crogels, has little influence on the coil-to-globule transition temperature of the PNIPAM chains<sup>52</sup>. The resulting microgels are made by two interpenetrated homopolymeric networks of PNIPAM and PAAc, with independent sensitivity to external stimuli, namely temperature and pH. In other words, the mutual interference between the temperature-responsive and pH-responsive polymers are weak enough to leave unchanged the temperature dependence of the VPT with respect to the case of pure PNIPAM microgel. This makes possible to directly control the microgel softness, indeed Mattson et al.<sup>16</sup> recently proposed a new approach in the use of PNIPAM-PAAc IPN microgel suspensions to explore how particle softness affects the fragility. They speculate that softer particles are more easily deformed, and as the particles shrink due to particle crowding, their shapes increasingly deviate from the spherical form, leading to an increased directionality of interparticle interactions, corresponding to strong behavior. In contrast, hard particles retain their spherical shape, and their interactions are more isotropic, corresponding to fragile behavior. Therefore IPN microgels are useful probes to explore the variation of fragility, due to the possibility to control its elasticity not only through the synthesis procedure, but also by tuning the PAAc content or, equivalently, the solution pH.

Indeed the different solubility of PAAc at acidic and neutral pH, introduces an additional control parameter, which allows to tune the mutual interference between PNIPAM and PAAc networks. At acidic pH the PAAc chains are not effectively solvated by water and H-bonds formation between the carboxylic (COOH-) groups of PAAc and the isopropyl (CONH-) groups of PNIPAM is favored, with respect to H-bonding with water molecules<sup>68</sup>. At neutral pH, the balance between PNIPAM/PAAc and water/PAAc H-bonds is reversed. Both compounds are therefore well solvated and water mediates their interaction, making the two networks completely independent one to each other.

The swelling behavior of aqueous suspensions of PNIPAM-PAAc IPN microgels as a function of temperature, pH and concentration has been extensively investigated by our group and the obtained results have been published elsewhere<sup>57,58</sup>. In particular in the high dilution regime, where the interparticle interactions are negligible and phase separation does not occur, a VPT around 305-307 K has been found, at both acidic and neutral pH, with a continuous or a sharp transition respectively, suggesting that H-bonding plays a non-trivial role.

In order to understand the role played by hydrophobicity and hydrogen bonding in the polymer-solvent interactions and in the dynamics of the polymer solutions, investigations of the isotopic effect give relevant information. Indeed it has been recently shown that a slowing down of the swelling kinetics and a shift forward of the VPTT of PNIPAM microgels occur in D<sub>2</sub>O suspensions with respect to H<sub>2</sub>O ones<sup>69</sup>, mainly due to the higher viscosity of the deuterated solvent. This is expected to affect also the elastic response of the IPN microgel particles.

In this work we present a DLS systematic investigation of the dynamics across the VPT of D<sub>2</sub>O compared to H<sub>2</sub>O suspensions of PNIPAM-PAAc IPN microgels, to explore how H-bondings affect the particle softness and therefore fragility. Furthermore we provide new insights into the unifying paradigm of fragility exploring the

effect of temperature and solvent.

## 2 Experimental Methods

### 2.1 Sample preparation

Detailed description of the materials and IPN microgel particles synthesis has been given in Ref.<sup>57,58</sup>. Once synthesized by a sequential free radical polymerization method, lyophilized IPN microgel samples were dispersed in D<sub>2</sub>O by magnetic stirring for 1 day. The sample was then lyophilized and redispersed again in D<sub>2</sub>O to obtain the final suspension at the required weight concentration. Samples at different concentrations were obtained by dilution with D<sub>2</sub>O.

### 2.2 DLS set-up and data analysis

DLS measurements have been performed with a multiangle light scattering setup. The monochromatic and polarized beam emitted from a solid state laser (100 mW at  $\lambda=642$  nm) is focused on the sample placed in a cylindrical VAT for index matching and temperature control. The scattered intensity is simultaneously collected at five different scattering angles, namely  $\theta=30^\circ, 50^\circ, 70^\circ, 90^\circ, 110^\circ$ , corresponding to five different scattering vector  $Q$ , according to the relation  $Q=(4\pi n/\lambda) \sin(\theta/2)$ . Single mode optical fibers coupled to collimators collect the scattered light as a function of time and scattering vector. In this way one can simultaneously measure the normalized intensity autocorrelation function  $g_2(Q, t) = \langle I(Q, t)I(Q, 0) \rangle / \langle I(Q, 0) \rangle^2$  at five different  $Q$  values with a high coherence factor close to the ideal unit value. Measurements have been performed as a function of temperature in the range  $T=(293 \div 313)$  K across the VPT at four different weight concentrations ( $C_w=0.10\%$ ,  $C_w=0.15\%$ ,  $C_w=0.20\%$ ,  $C_w=0.32\%$ ), at both acidic and neutral pH. Reproducibility has been tested by repeating measurements several times.

Fig.1 shows the typical behavior of the normalized intensity autocorrelation functions for an IPN sample at weight concentration  $C_w=0.32\%$  (Fig.1(a)) and  $C_w=0.10\%$  (Fig.1(b)) and pH 7, collected by a detector at  $\theta=90^\circ$  with respect to the incident beam.

As commonly known, the intensity correlation function of most colloidal systems is well described by the Kohlrausch-Williams-Watts expression<sup>70,71</sup>:

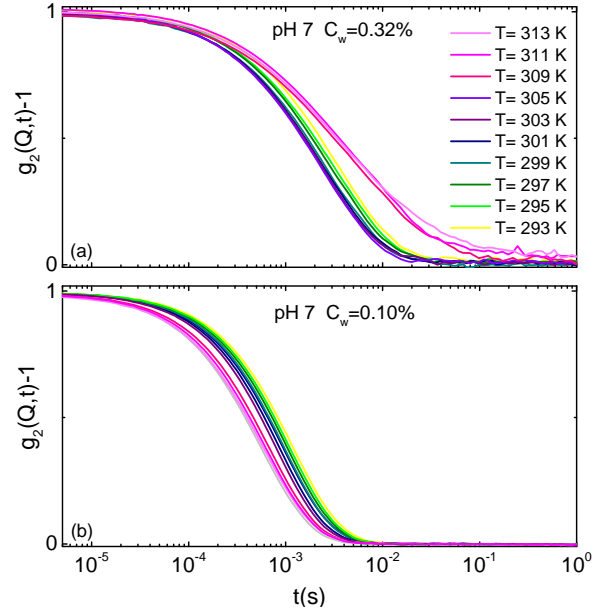
$$g_2(Q, t) = 1 + b[(e^{-t/\tau})^\beta]^2 \quad (1)$$

where  $b$  is the coherence factor,  $\tau$  is an "effective" relaxation time and  $\beta$  describes the deviation from the simple exponential decay ( $\beta = 1$ ) usually found in monodisperse systems and gives a measure of the distribution of relaxation times. Many glassy materials show a stretching of the correlation functions (here referred to as "stretched behavior") characterized by an exponent  $\beta < 1$ .

## 3 Results

### 3.1 Isotopic effect on the dynamics

In Fig.2 the comparison between the temperature dependence of the relaxation time and the parameter  $\beta$ , as obtained through a fit with Eq.(1) for D<sub>2</sub>O and H<sub>2</sub>O suspensions, at (a) pH 5 and (b) pH 7, is reported at two fixed concentrations as an example. In D<sub>2</sub>O

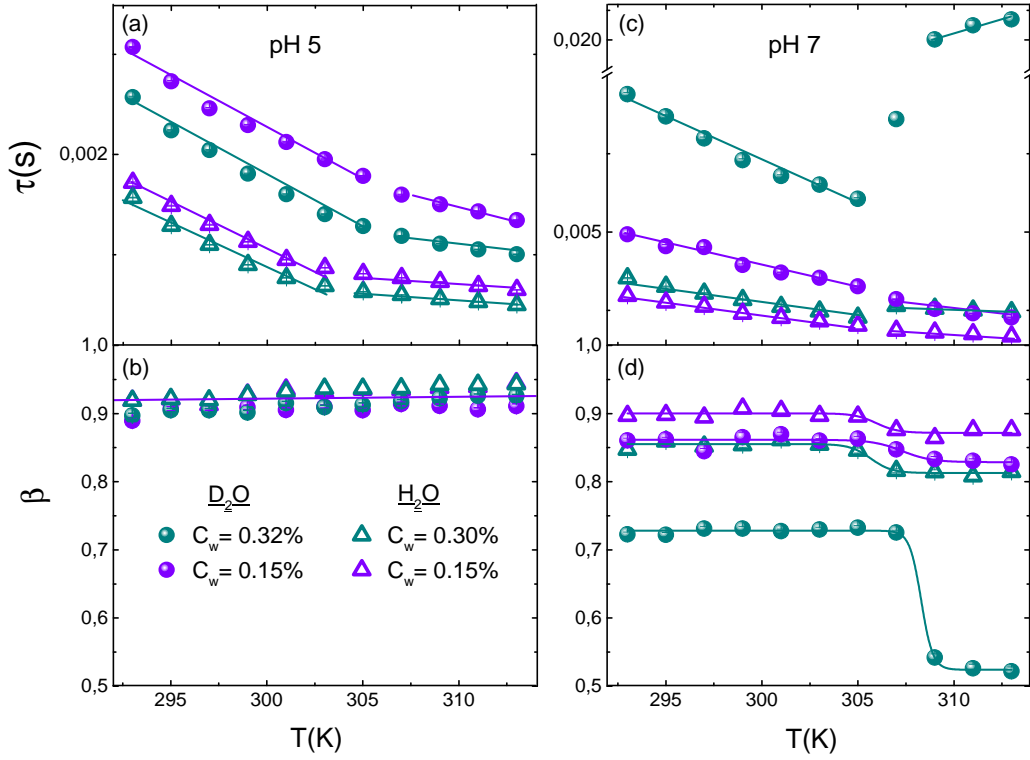


**Fig. 1** Normalized intensity autocorrelation function of a D<sub>2</sub>O suspension of IPN microgels at (a)  $C_w=0.32\%$  and (b)  $C_w=0.10\%$ , at pH 7 and  $\theta=90^\circ$  for the indicated temperatures.

a dynamical transition associated to the VPT, from a swollen to a shrunken state, is evidenced as for H<sub>2</sub>O suspensions<sup>57</sup>. At acidic pH (Fig. 2(a)) the relaxation time slightly decreases as temperature increases, until the transition is approached around  $T=305$  K. Above this temperature the relaxation time decreases to its lowest value, corresponding to the shrunken state, evidenced by a change of the slope. Moreover the stretching parameter  $\beta$  (Fig. 2(b)) does not change with temperature and concentration and indicates slightly stretched correlation functions ( $\beta \approx 0.9$ ).

This behavior is strongly affected by the pH of the solution, as shown in Fig.2(c) at pH 7, where the H-bonds interactions between the carboxylic groups of PAAc and PNIPAM are reduced. In particular, as temperature increases, the relaxation time slowly decreases up to the VPTT; above this temperature, different behaviors are observed, depending on concentration. At low concentration ( $C_w=0.15\%$ ) the relaxation time always decreases, whilst a swap in trend at the highest concentrations ( $C_w=0.32\%$ ) is observed and the relaxation time reaches its highest values. At the same time the stretching parameter  $\beta$ , at variance with the case of pH 5, decreases with concentrations. As for the relaxation time, different behavior are observed above the VPTT: at low concentration  $\beta$  does not change with temperature, while at the highest concentration it decreases to values  $\beta \approx 0.5$  (Fig.2(d)), corresponding to a clear change of the shape of the intensity autocorrelation functions, well evidenced in Fig.1(a).

Although the main features of the swelling behavior typical of PNIPAM-PAAc IPN microgels in H<sub>2</sub>O suspensions<sup>57</sup> are preserved under isotopic substitution, interesting differences between D<sub>2</sub>O and H<sub>2</sub>O samples are observed, as evidenced in Fig.2. The relaxation times are always higher in D<sub>2</sub>O than in H<sub>2</sub>O, at all pH and concentrations, suggesting a slowing down of the dynamics under isotopic substitution, probably due to the higher viscosity of



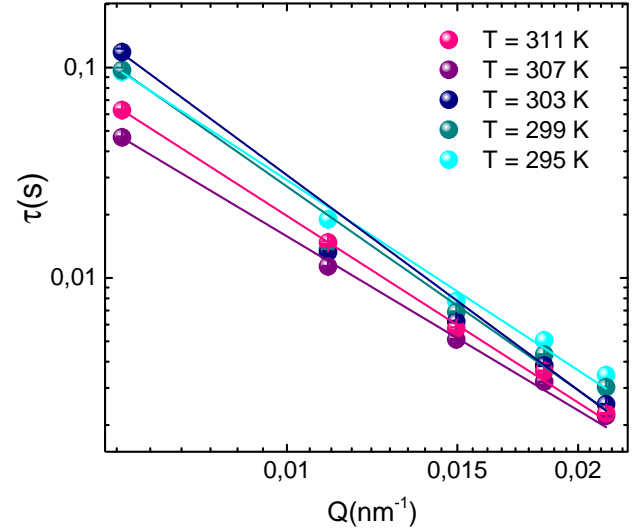
**Fig. 2** (a) Relaxation time and (b) stretching parameter as a function of temperature for D<sub>2</sub>O and H<sub>2</sub>O suspensions of IPN microgels at the indicated concentrations and pH 5. (c) Relaxation time and (d) stretching parameter as a function of temperature for D<sub>2</sub>O and H<sub>2</sub>O suspensions of IPN microgels at the indicated concentrations and pH 7. Full lines are guides for eyes.

D<sub>2</sub>O compared to H<sub>2</sub>O. In the investigated temperature region, the range of variability of the relaxation time is almost twice in D<sub>2</sub>O compared to H<sub>2</sub>O (Fig.2(a)). Moreover at pH 5 a shift of the VPTT to higher temperature with respect to H<sub>2</sub>O is observed. On the contrary, at pH 7 the VPT occurs at the same temperature in both solvents, confirming that pH affects the role played by H-bondings. Finally, at neutral pH and at the highest concentration the jump of the relaxation time to higher values above the VPTT, is greatly amplified under H/D isotopic substitution, as evidenced in Fig.2(b) for H<sub>2</sub>O<sup>57</sup> and D<sub>2</sub>O samples. The  $\beta$  parameter is significantly affected by isotopic substitution only for the highest concentration at pH 7, as evident from its lower values and the jump across the VPTT.

In order to obtain additional information on the dynamical behavior of D<sub>2</sub>O IPN microgel suspensions, the relaxation time and the stretching parameter have been investigated at different length scales, as a function of the scattering vector  $Q$ . In Fig.3, an example at  $C_w=0.10\%$  and pH 7, is reported. The relaxation time is strongly  $Q$  dependent and can be described by a typical power law decay:

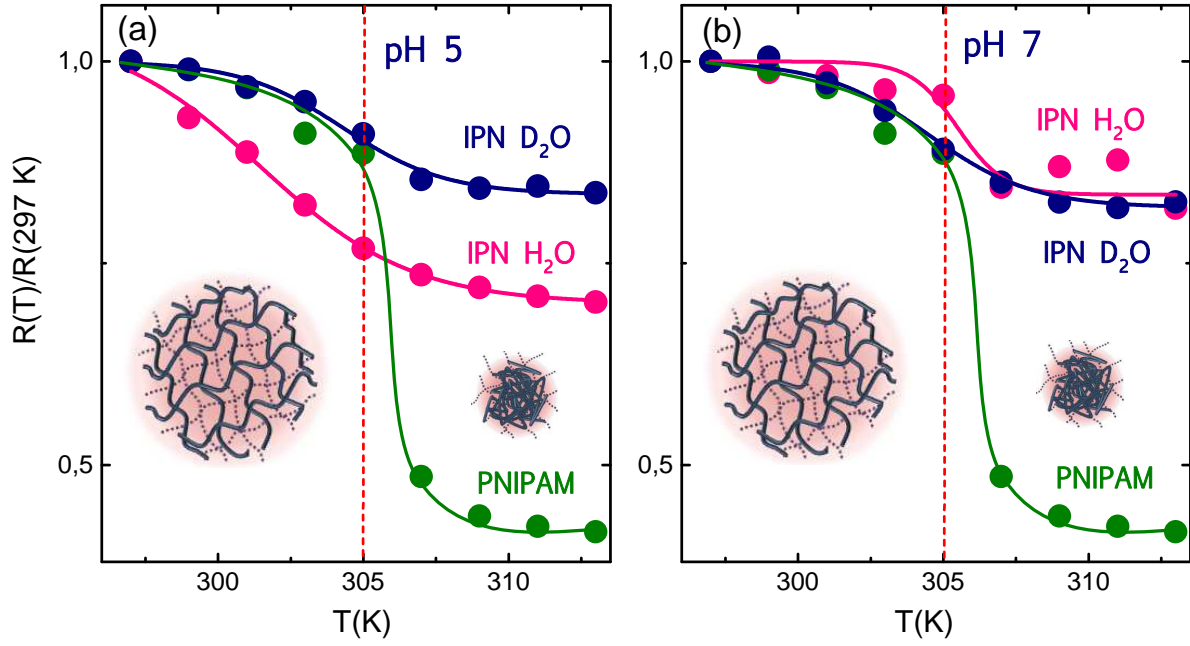
$$\tau = A Q^{-n} \quad (2)$$

where  $A$  is a constant and the exponent  $n$  defines the nature of the motion. The fits according to Eq.(2) are superimposed to the data as full lines in Fig.3. The exponent  $n$  is found between 2 and 4, for all concentrations and temperatures in agreement with the results of Mattsson et al.<sup>16</sup> at fixed temperature and as pre-



**Fig. 3** (a) Relaxation time as a function of scattering vector  $Q$  at  $C_w=0.10\%$ , pH 7 for the indicated temperatures. Full lines are fits through Eq.(2) with  $n=2.94\pm0.03$  ( $T=311$  K),  $n=2.749\pm0.002$  ( $T=307$  K),  $n=3.395\pm0.007$  ( $T=303$  K),  $n=3.217\pm0.006$  ( $T=299$  K),  $n=3.004\pm0.003$  ( $T=295$  K).

viously observed for H<sub>2</sub>O IPN microgels suspensions<sup>57</sup>. Similar results have already been published for different polymers<sup>72,73</sup>, although a theoretical background to explain this dependence is not yet available. Meanwhile the stretching parameter  $\beta$  does not show any dependence on the scattering vector  $Q$ . The  $Q$ -dependence of the relaxation time and the stretching parameter



**Fig. 4** Normalized radius as obtained from DLS measurements for an IPN microgels in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  suspensions at  $C_w = 0.10\%$ , (a) pH 5 and (b) pH 7, compared with the normalized radius obtained for PNIPAM microgels. Full lines are guides for eyes.

of  $\text{D}_2\text{O}$  IPN microgels suspensions confirms the behavior observed in  $\text{H}_2\text{O}$  suspensions.

All these findings can be well summarized through the temperature dependence of the normalized hydrodynamic radii of IPN microgels in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  suspensions at pH 5 (Fig. 4(a)) and pH 7 (Fig. 4(b)), compared with PNIPAM microgels at the same weight concentration ( $C_w = 0.10\%$ ). They have been calculated, according to the Stokes-Einstein relation for Brownian particles in the high dilution limit, as  $R = K_B T / 6\pi\eta D_t$ , where  $D_t$  is the translational diffusion coefficient calculated from  $\tau$  through the relation  $\tau = 1/Q^2 D_t$ . The sample viscosity  $\eta$  has been approximated with the solvent one and the radii have been normalized with respect to their values at  $T = 297\text{ K}$ . Fig. 4 evidences a clear reduction of the swelling capability of IPN microgels in both solvents compared to PNIPAM microgel, thus confirming that the presence of the acrylic acid reduces the swelling capability of the microgel particles also in deuterated suspensions<sup>51,55,56</sup>. Nevertheless different behaviors depending on solvent and pH are observed. For  $\text{D}_2\text{O}$  suspensions at acidic pH the transition appears sharper and the range of variability of  $R$  is reduced with respect to  $\text{H}_2\text{O}$ , while at neutral pH the transition is smoother and the range of variability of  $R$  is the same. Moreover while in  $\text{H}_2\text{O}$  a clear difference is observed between the normalized radii at acidic and neutral pH, no significant changes are evident in  $\text{D}_2\text{O}$ . This suggests that the balance between polymer/polymer and polymer/solvent interactions strictly depends on the solvent and therefore on the H-bondings.

### 3.2 Fragility in $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ suspensions of IPN microgels

It is well known that the structural relaxation time and the viscosity grow many order of magnitude with decreasing temperature when the glassy state is approached in supercooled molecular liquids<sup>17</sup>. The rapidity with which these quantities increase can be quantified

by the fragility index  $m$  defined as

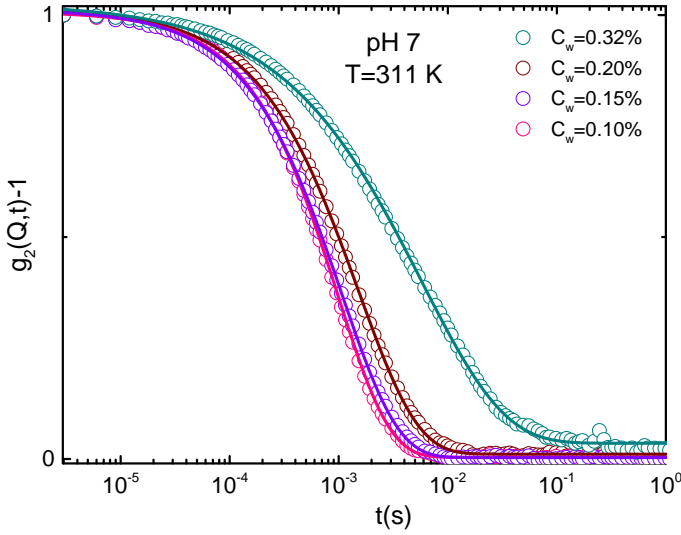
$$m = \left[ \frac{\partial \log \tau}{\partial (T_g/T)} \right]_{T=T_g} \quad (3)$$

where  $\tau$  is the relaxation time and  $T_g$  is the glass transition temperature. "Fragile" liquids are highly sensitive to changes in  $T$ , while "strong" liquids have a much lower  $T$  sensitivity, with respectively a super-Arrhenius (Vogel Fulcher Tammann expression) and an Arrhenius behavior of the relaxation time and viscosity with decreasing temperature. This unifying concept describes and classifies the glassy behavior of glass forming systems<sup>17,18,74</sup>. The same concept has been extended to colloidal systems where the glass transition occurs by increasing the volume fraction<sup>16,19</sup>.

Indeed it has been recently shown by Mattsson et al.<sup>16</sup> that the fragility of soft colloidal particles is related to their elastic properties. They studied IPN microgel suspensions in water at different concentrations and fixed temperature. In our work we extend the investigation at different temperatures and solvents.

The concentration dependence of the dynamics of IPN microgel suspensions is highlighted in Fig. 5, where the normalized intensity autocorrelation functions at fixed temperature ( $T = 311\text{ K}$ ) and pH 7 are reported. The observed behavior indicates that, as concentration increases, the decay become more and more stretched, as well evidenced in Fig. 6, where the concentration behavior of the stretching parameter  $\beta$  at fixed temperatures ( $T = 295\text{ K}$  and  $T = 311\text{ K}$ ) and pH 7, is reported for both  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  suspensions. We find that  $\beta$  continuously decreases with concentration without approaching the constant trend, as found by Mattsson et al.<sup>16</sup>, suggesting that we are well below the critical value, which they defined as the cross-over concentration from a monomodal to a bimodal behavior. Moreover this decrease is enhanced in  $\text{D}_2\text{O}$  and above the VPTT ( $T = 311\text{ K}$ ).





**Fig. 5** Normalized intensity autocorrelation function of a D<sub>2</sub>O suspension of IPN microgels at fixed temperature ( $T=311$  K) and pH 7 for the indicated concentrations. Lines superimposed to data are fits according to Eq.(1).

In Fig.7 the comparison between the concentration dependence of the relaxation time at acidic pH (Fig.7(a)) and neutral pH (Fig.7(b)) is reported. At pH 5 and fixed temperature,  $\tau$  linearly decreases as concentration increases, while at pH 7 the relaxation time exhibits an inverted trend with a non-linear increase with concentration and a faster rise at the highest temperature ( $T=311$  K). The different behavior observed at pH 5 and pH 7 suggests that the presence of PAAc hugely affects the dynamics of the system. In particular at neutral pH an exponential increase is found for the relaxation time, both below and above the VPT.

We found that the exponential dependence below the VPT is well fitted with an Arrhenius behavior, typically observed in strong molecular glass-formers, where  $C_w$  plays the role of  $1/T$ . Therefore at these temperatures data are well described by the relation

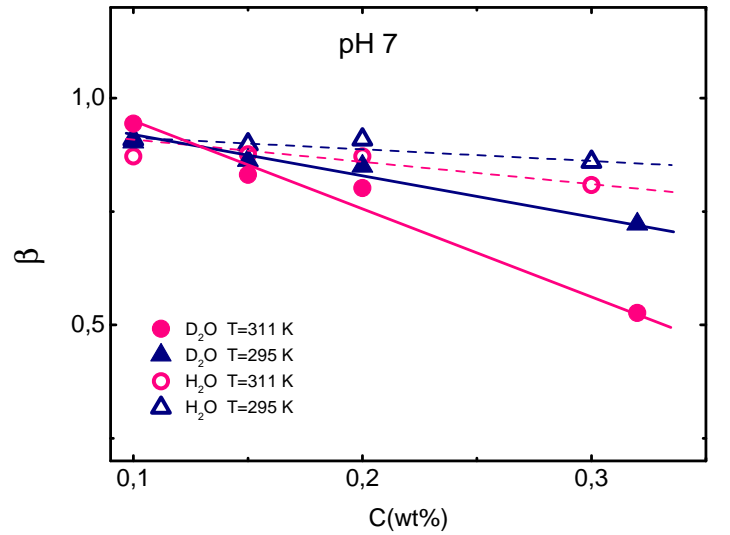
$$\tau = \tau_0 e^{AC_w} \quad (4)$$

where  $A$  is a constant and  $\tau_0$  is the characteristic relaxation time for low values of  $C_w$ . On the other hand the relaxation time behavior at temperature above the VPTT can be described via the Vogel-Fulcher-Tammann (VFT) expression, where again  $C_w$  replace  $1/T$ :

$$\tau = \tau_0 e^{\frac{AC_w}{C_0 - C_w}} \quad (5)$$

where  $C_0$  sets the apparent divergence,  $A$  controls the growth of the relaxation time on approaching  $C_0$  and  $\tau_0$  is the characteristic relaxation time at low concentrations. These functions provide a good description of the concentration dependence of  $\tau$ , thus confirming that the paradigm for supercooled molecular liquids near their glass transition can be extended to suspensions of soft particles, where the concentration  $C_w$  plays a role analogous to the inverse of temperature  $1/T$  in molecular systems.

Generally the concept of fragility is summarized in a renormalized Arrhenius plot, where the temperature is rescaled by the glass-transition temperature,  $T_g$ , and fragility is defined by the logarith-

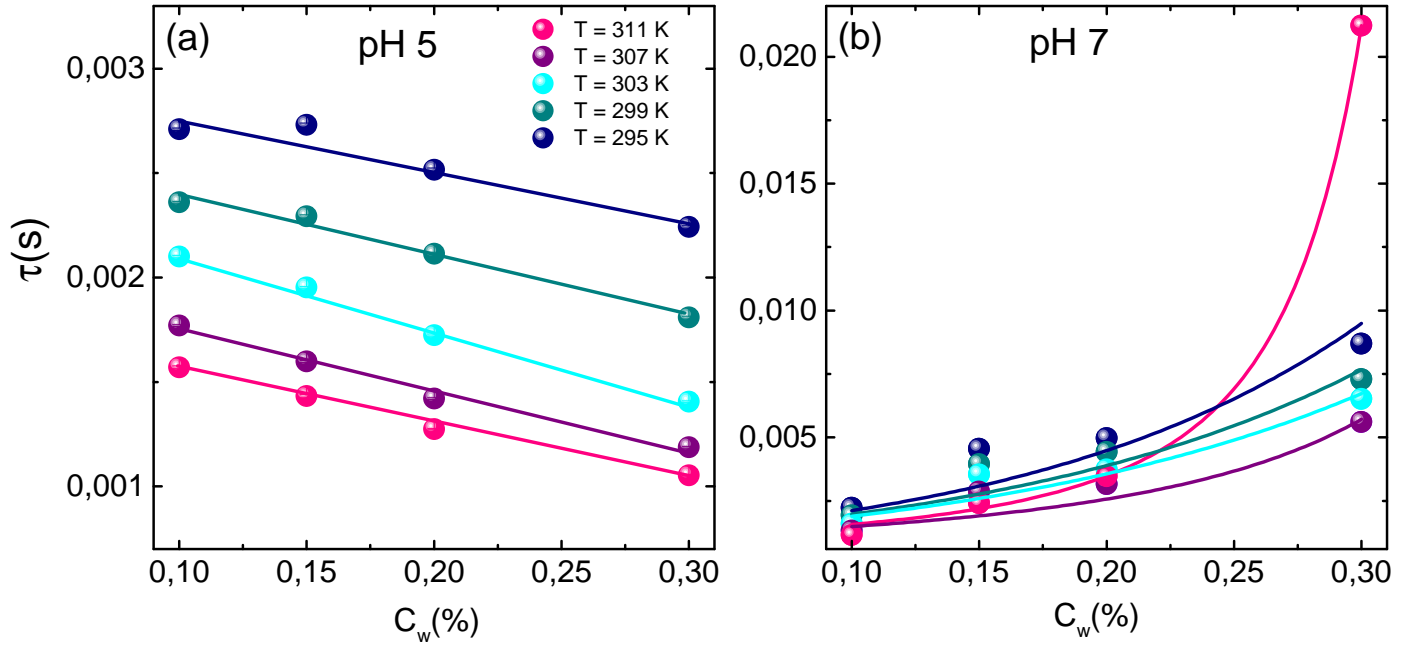


**Fig. 6** Stretching coefficient as obtained from normalized intensity autocorrelation function for D<sub>2</sub>O and H<sub>2</sub>O suspensions of IPN microgels at fixed temperature ( $T=311$  K) and pH 7 for the indicated concentrations. Full (D<sub>2</sub>O) and dashed (H<sub>2</sub>O) lines are guides for eyes.

mic slope at  $T_g$ <sup>17</sup>. This representation provides a unifying framework to describe the variation from strong to fragile behavior of molecular liquids. According to Mattsson et al.<sup>16</sup>, we explore the analogy between soft colloidal suspensions and molecular glass-formers by rescaling the Arrhenius plot in a fashion similar to that used for molecular glasses. Indeed the corresponding plot for colloids can be obtained by scaling  $C_w$  by the "glass concentration"  $C_g$ , defined as the concentration  $C_w(\tau = 100$  s), where the structural relaxation time is no longer experimentally accessible<sup>18</sup>. In this way we obtain a renormalized Arrhenius plot for D<sub>2</sub>O and H<sub>2</sub>O suspensions, as shown in Fig.8 at pH 7, where only two temperatures are reported since all data below the VPTT collapse on  $T=295$  K and all data above collapse on  $T=311$  K. The slope of the data at  $C_w = C_g$  defines the fragility:

$$m = \left[ \frac{\partial \log \tau}{\partial (C_w/C_g)} \right]_{C_w=C_g} \quad (6)$$

As discussed before the most fragile materials are those that show the largest deviations from the Arrhenius law. In our case we observe that both in D<sub>2</sub>O and H<sub>2</sub>O for all temperatures below the VPT, in the swollen state, soft IPN microgels behave as strong materials. On the contrary above the VPT, in the shrunken state, they become stiff and behave as fragile systems. Moreover in this case the fragility of the system can be tuned by changing the solvent. In particular for all  $T < VPTT$  we find  $m = 26.5$  in both H<sub>2</sub>O and D<sub>2</sub>O suspensions and for all  $T > VPTT$ , we find  $m = 30.6$  in H<sub>2</sub>O and  $m = 40.8$  in D<sub>2</sub>O, where higher values of  $m$  correspond to stiffer particles. This means that across the VPT the system encompasses a transition from a strong to a fragile behavior in both solvents. Nevertheless we find that above the VPT, microgel particles in D<sub>2</sub>O suspensions are stiffer than in H<sub>2</sub>O, thus leading to a more fragile behavior. Interestingly, this observation is reminiscent of that seen for the concentration behavior of  $\beta$ , where lower values cor-



**Fig. 7** Relaxation times as a function of the weight concentration at fixed temperatures at (a) pH 5 and (b) pH 7 for D<sub>2</sub>O suspensions. Full lines in (a) are linear fits and full lines in (b) are fits according to Eq.4 below the VPTT and Eq.5 above the VPTT.

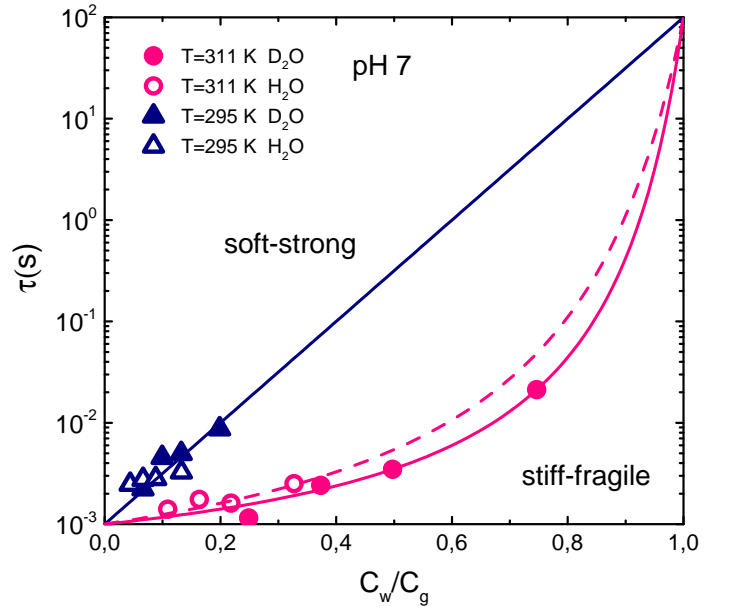
responds to stiffer particles and therefore to more fragile behaviors. At variance with previous studies, where the fragility of the particles was varied by changing the polymeric networks, here we are able to pass from a strong (soft) to fragile (stiff) behavior on a single system by changing temperature below and above the VPT.

These results confirm that the observed fragility of colloidal particles increases as softness decreases, according to the experimental results by Mattsson et al.<sup>16</sup>. Therefore our results may give an additional improvement to the investigation of the connection between the fragility of colloids and the softness of the potential, thanks to the possibility to modulate the inherent softness of the microgel particles by changing temperature and/or solvent. This point, still controversial, calls for further investigation to reconcile the differences among experimental, numerical and theoretical results.

## 4 Conclusions

The effect of the H/D isotopic substitution on the swelling behavior of PNIPAM-PAAc IPN microgels has been investigated as a function of temperature, pH, concentration and scattering vector by comparing new experiments on deuterated suspensions with previous findings on IPN microgels in H<sub>2</sub>O<sup>57</sup>.

It has been shown that H/D isotopic substitution in the solvent plays an important role on the kinetics of the swelling, affecting its time scale, although preserving the same physical properties observed in H<sub>2</sub>O. In particular a reduced swelling capability with respect to PNIPAM microgels confirms our findings for H<sub>2</sub>O suspensions. The relaxation time is almost twice that typical of H<sub>2</sub>O IPN microgels and at acidic pH the VPTT is shifted to higher temperatures, indicating a slowing down of the swelling kinetics in D<sub>2</sub>O. Moreover the range of variability of  $\tau$  is greatly enhanced in D<sub>2</sub>O and the pH dependence is reduced with respect to D<sub>2</sub>O, as



**Fig. 8** Arrhenius plot for the relaxation time  $\tau$  versus concentration  $C_w$  normalized by  $C_g = C_w(\tau(100s))$  at  $T=295$  K (triangles) and  $T=311$  K (circles) for D<sub>2</sub>O (solid symbols) and H<sub>2</sub>O (open symbols). Lines superimposed to data are fits according to the Arrhenius (black line) and the VFT (orange line) equations, for soft and stiff particles, respectively.

evidenced by the temperature behavior of the normalized hydrodynamic radius.

Therefore our results suggest that hydrogen-bonds play a crucial role in the polymer-solvent interactions and that the swelling kinetics can be slightly affected by D<sub>2</sub>O. In this case, indeed, stronger H-bondings occur between polymer and solvent with respect to the case of H<sub>2</sub>O, hence changes in the rate of the swelling/shrinking

transition were expected<sup>69</sup>. Importantly at the highest concentrations and at pH 7, we have found a clear enhancement of the transition of the relaxation time to higher values above the VPTT compared to the case of H<sub>2</sub>O. This behavior can be interpreted as a precursor of the more complex behavior expected at even higher concentrations, where a non-ergodic transition is expected to occur.

Moreover we confirm the hypothesis of Mattsson et al.<sup>16</sup> that the universal framework of fragility can be extended to colloidal systems by controlling the particle elasticity. In addition we find that the elastic response of IPN microgel suspensions can be modulated by changing temperature: below the VPT the particles are soft and deformable, whilst above the VPT they become stiff and undeformable. This is associated to increasing values of fragility, which suggests that the swelling/shrinking behavior drives the system through a transition from strong to fragile. Therefore fragility has to be strictly related to the VPT: soft particles will lead to strong behavior and stiff particles to fragile behavior. In addition the different concentration dependence observed in H<sub>2</sub>O and D<sub>2</sub>O suspensions suggests that fragility is also affected by the solvent, as a consequence of the different balance between polymer/polymer and polymer/solvents interactions. In D<sub>2</sub>O a more fragile behavior above the VPT is observed, indicating that IPN microgel particles reach their highest degree of stiffness upon shrinking.

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